Process-Property-Structure Relationships in Complex Oxide Melts

Richard Weber and Paul Nordine
Containerless Research, Inc.
Evanston, IL 60201-3149

Phone: (847) 467-2678
email: weber@containerless.com

Introduction and Background

Investigation of process-property-structure relationships in high temperature liquids is essential to a scientific understanding of the liquid state and technological advances in liquid-phase processing. This research is concerned with the effects of processing variables on the behavior and properties of molten oxides. It uses containerless experimental methods to eliminate container-derived contamination, allow equilibration with controlled $p(O_2)$ atmospheres, and avoid heterogeneous nucleation by container walls to access highly non-equilibrium liquids.

Research during the first two years (June 1996-June 1998) included investigation of binary alumina-silica (Al_2O_3-SiO_2) and alumina-yttria (Al_2O_3-Y_2O_3) materials. Strong emphasis has been placed on investigation of the alumina-yttria compositions because they form melts which display an anomalous increase in viscosity when they are undercooled. The alumina-yttria system is a promising candidate for low gravity experiments to measure the melt viscosity and investigate liquid phase transitions and the onset of increased viscosity in the liquid. Low gravity experiments are being developed in a separate Flight Definition project.

Accomplishments to date were to:

1. Investigate liquid-phase processing, undercooling, and solidification of binary alumina-silica and alumina-yttria materials as a function of composition, ambient $p(O_2)$, and thermal history.

2. Investigate the anomalous increase in the viscosity observed in deeply undercooled melts.

3. Measure of the enthalpy of solution of compounds formed by containerless cooling of melts and determine the enthalpy of vitrification of YAG-composition liquid.

4. Characterize processed materials using optical and scanning electron microscopy and X-ray diffraction analysis.

Experimental Methods

Spheroidal specimens *ca.* 0.3 cm. in diameter were made by laser hearth melting of high purity oxide powders. Specimens were levitated in an aero-acoustic or aerodynamic levitator in argon or oxygen and melted using cw CO_2 laser beam heating. The compositions investigated contained 40-90 mole % alumina with 10-60 mole % silica, and 61.5-79.0 mole % alumina with 21.0-38.5 mole % yttria. Materials containing erbium and neodymium oxide substituted for yttium oxide were also investigated.

Results

1. *Liquid-Phase Processing Experiments:* Compositions centered around $Y_3Al_5O_{12}$ followed different solidification paths depending on the process conditions. Melts processed in oxygen undercooled by 800-900 °C and spontaneously crystallized to form yttrium aluminum garnet, or undercooled by 600-650 °C and spontaneously crystallized to form a mixture of perovskite and aluminum oxide. Crystallization of YAG was favored if the liquid was superheated by >200°. Stoichiometric melts processed in argon also crystallized, but formed glass if they contained a small excess of alumina or some neodymium substituted for yttrium. However, glass of the stoichiometric composition could also be formed in argon at the much larger cooling rates achieved in fiber pulling experiments.

2. *Investigation of Melt Viscosity:* Glass formation from the YAG-composition shows that the viscosity of the melt can increase greatly when it is deeply undercooled. Experiments to pull fibers from the undercooled liquid show that the onset of increased viscosity occurs at a temperature about 600° below the equilibrium melting point.

3. *Enthalpy Measurements on Solidified Materials:* Solution calorimetry experiments were performed on processed materials by Dr. I-Ching Lin and Professor Alexandra Navrotsky at Princeton University. We conclude that formation of the yttrium aluminum garnet phase is thermodynamically favored over a mixture of perovskite and alumina: the enthalpy for the reaction, $3\ YAlO_3 + Al_2O_3 = Y_3Al_5O_{12}$ is $\Delta H^\circ_{298} = -32.14$ kJ/mol. However, perovskite is observed to form from the undercooled melt due to kinetic limitations on attaining the garnet structure. The enthalpy of vitrification of the garnet form was calculated to be 276.47 kJ/mol or 13.82 kJ/g.atom. The heat of fusion of YAG was estimated to be 516 kJ/mol.

Plans

The goal of the ongoing research is to understand the nature of changes in undercooled molten oxides which lead to the onset of increased viscosity. Several avenues will be pursued including: (i) investigation of melt viscosity using drop oscillation techniques; (ii) investigation of the structure of undercooled molten YAG using containerless techniques in combination with synchrotron radiation; and, (iii) *in-situ* measurements of the vapor species as a function of composition and process conditions to determine the component activity variations that occur in the liquid.